

Department of Aerosols and Laser Studies

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LAB TECHNICIANS

DARIA BARTLOVÁ

Fields of research

- Atmospheric aerosols
- Indoor/outdoor aerosols
- Nucleation phenomena
- Synthesis of nanoparticles *via* aerosol processes
- Heat and mass transfer in aerosol systems
- Interaction of aerosols with electromagnetic radiation
- Emissions sampling
- Nanoparticles and health
- Aerosol technology
- IR and UV laser induced chemistry
- Chemical vapor deposition of novel C-, Si- and Ge-based nanostructured materials
- IR laser-induced carbothermal reduction of oxides
- UV laser deposition of SERS active substrates based on Ag/graphene
- CVD of nanostructured objects (nanowires, nanoplatelets)
- IR and UV laser deposition of Ti/O-based materials
- IR and UV laser ablation for deposition of thin films, multilayers and nanocomposites

Research projects

Human EXposure to Aerosol COnaminants in Modern Microenvironments

(J. Smolík, smolik@icpf.cas.cz and V. Ždímal, zdimal@icpf.cas.cz; supported by EC, Marie Curie Actions - Initial Training Networks, project No. 315760, FP7-PEOPLE-2012-ITN, HEXACOMM, project partner)

The main research goal of HEXACOMM is to apply scientifically-based modelling and experimental methods to relate concentrations of particulate matter in the indoor domestic environment to its sources and human exposure implications. The second research objective is to determine the human exposure arising from such exposure at both individual and collective (population) scales at modern microenvironments.

Contributions from outdoor air will be taken into account. Central idea of HEXACOMM is that a combination of tools and methods will enable us to relate indoor air quality to aerosol contaminants in urban homes, offices, vehicles with human exposure in a quantitative manner. To achieve our goal and objectives we propose to undertake, in parallel, a carefully designed validation programme at the European scale combining specifically targeted indoor air quality measurements, source apportionment studies, micro-environmental modelling, dosimetry modelling and exposure studies. Ultimately, our vision is that such enhanced understanding of the underpinning science will lead to improved indoor air quality in European domestic environments, while facilitating development of strategies to mitigate the impacts of aerosols on human exposure.

Aerosols, Clouds, and Trace gases Research Infra Structure Network

(V. Ždímal, zdimal@icpf.cas.cz; supported by EC, project No. INFRA-2010-1.1.16 ACTRIS, as "initial associated partner")

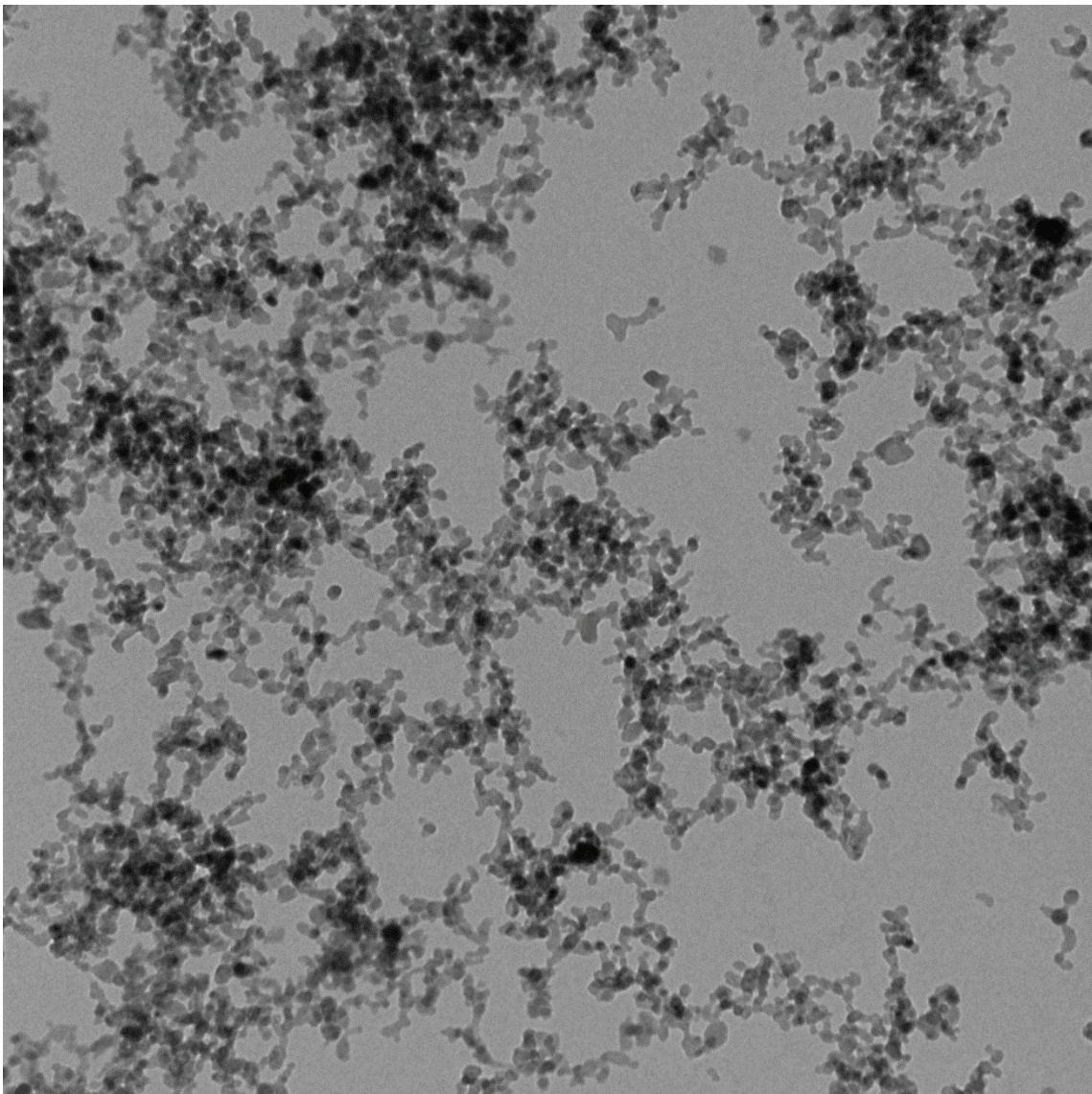
ACTRIS (Aerosols, Clouds, and Trace gases Research Infra Structure Network) is an European Project aiming at integrating European ground-based stations equipped with advanced atmospheric probing instrumentation for aerosols, clouds, and short-lived gas-phase species. ACTRIS will have the essential role to support building of new knowledge as well as policy issues on climate change, air quality, and long-range transport of pollutants.

ACTRIS is building the next generation of the ground-based component of the EU observing system by integrating three existing research infrastructures: EUSAAR, EARLINET, CLOUDNET, and a new trace gas network component into a single coordinated framework. ACTRIS is funded within the EC FP7 under "Research Infrastructures for Atmospheric Research". [Refs. 1, 13]

Centre for studies on toxicity of nanoparticles

(P. Moravec, moravec@icpf.cas.cz; supported by GACR, project No. P503/12/G147)

The rapid expansion of nanomaterials production and their use in many products create a need for understanding the mechanisms of nanomaterial interactions with living systems. This need is above all given by unique properties of nanoparticles related to their dimensions and by their ability to penetrate into various tissues and cells in organism. Nanoparticles are also formed unintentionally as a result of the anthropogenic activities (industry, local heating). The proposed interdisciplinary centre of basic research will integrate laboratories capable to perform complex studies on mechanism of the toxicity of important and widely used engineered nanoparticles, as well as anthropogenic nanoparticles in the environment with a special attention paid to heavily polluted areas of the Czech Republic. The studies will be performed on thoroughly characterized nanoparticles to obtain valid and comparable results on biological action and toxicity of nanoparticles.



TEM image of TiO₂ (anatase) nanoparticles generated for inhalation experiments by thermal decomposition of titanium tetra-isopropoxide at $T_R=900\text{ }^\circ\text{C}$, $Q_R=1200\text{ cm}^3/\text{min}$, $P_{\text{TTIP}}=1.9\text{ Pa}$, image area $1.36\times 1.36\text{ }\mu\text{m}$. Notice quite uniform nanoparticles with typical size $12 - 20\text{ nm}$

Thermophysical properties of water in unexplored, technologically significant regions
(V. Ždímal, zdimal@icpf.cas.cz; joint project with Institute of Thermomechanics of the ASCR, CTU, and University of West Bohemia, Plzeň; supported by GA ASCR, project No. IAA4200760905)

This project focuses primarily on liquid water and solutions of selected salts below the freezing point (supercooled water), and water in nano-droplets. Existing hypotheses include the possibility of phase separation of supercooled water into two liquid phases below the second critical point. Density of supercooled water is only known at 0.1 MPa. Suggested measurements up to 100 MPa will provide first data. A new method and apparatus will be developed. The surface tension of supercooled water and a salt solution will be measured. The surface tension of nano-droplets will be estimated from nucleation experiments. A range of theoretical approaches including phenomenological methods, simplified microscopic models, and molecular simulations, will be used with experimental data to obtain fundamental findings and engineering models. [Refs. 11, 12, 17, 18, 22, 23]

Advanced study of physical and chemical properties of atmospheric aerosols in high time resolution

(V. Ždímal, zdimal@icpf.cas.cz; supported by GACR, project No. 209/11/1342)

Advanced physical and chemical properties of Central European atmospheric aerosol at rural background and urban background sites will be studied in high time and size resolution. Parallel measurement of aerosol volatility will be carried out using a C-ToF-AMS equipped with a thermodenuder inlet, aerosol hygroscopicity using an Hygroscopic Tandem Differential Mobility Analyser (HTDMA), and particle number size distribution using an Scanning Mobility Particle Sizer (SMPS). The information about aerosol particle density will be extracted from the SMPS and AMS. Hygroscopicity closure will be obtained from the combined HTDMA and AMS chemical composition data allowing to study the influence of organic aerosol on particles' hygroscopicity. The content of primary and secondary organic aerosol and the extent of aerosol ageing will be determined using AMS data at each site. In addition, at least a year-long time evolution of number size distributions obtained using the SMPS and OC/EC concentrations from the OC/EC analyzer will be delivered to the EBAS database, to be available for global atmospheric modeling groups. [Refs. 19, 21]

Development and application of new experimental methods to measure heterogeneous particles in superheated steam

(V. Ždímal, zdimal@icpf.cas.cz; joint project with CTU and Institute of Thermomechanics of the ASCR; supported by GACR, project No. 101/09/1633)

The aim of the project is to determine some properties of heterogeneous nuclei present in the superheated steam of steam turbines. In this project, the sampling device, coupled to advanced aerosol instrumentation (condensation particle counter, scanning mobility particle sizer), will be used to measure heterogeneous particles at selected power stations. To enable measurements of particles down to about 1 nm, a fast expansion chamber will be developed, enabling resolution of particle size by variable supersaturation. Collected data will serve as a basis for understanding the transport and the state of agglomeration of chemicals present in the steam circuit, for quantifying their effect on condensation, and, consequently, on the efficiency and reliability of steam turbines. [Ref. 8]

Black and elemental carbon at two European urban sites – site specific similarities and differences in method intercomparability

(J. Schwarz, schwarz@icpf.cas.cz; supported by MEYS, program MOBILITY, project No. 7AMB12AT021)

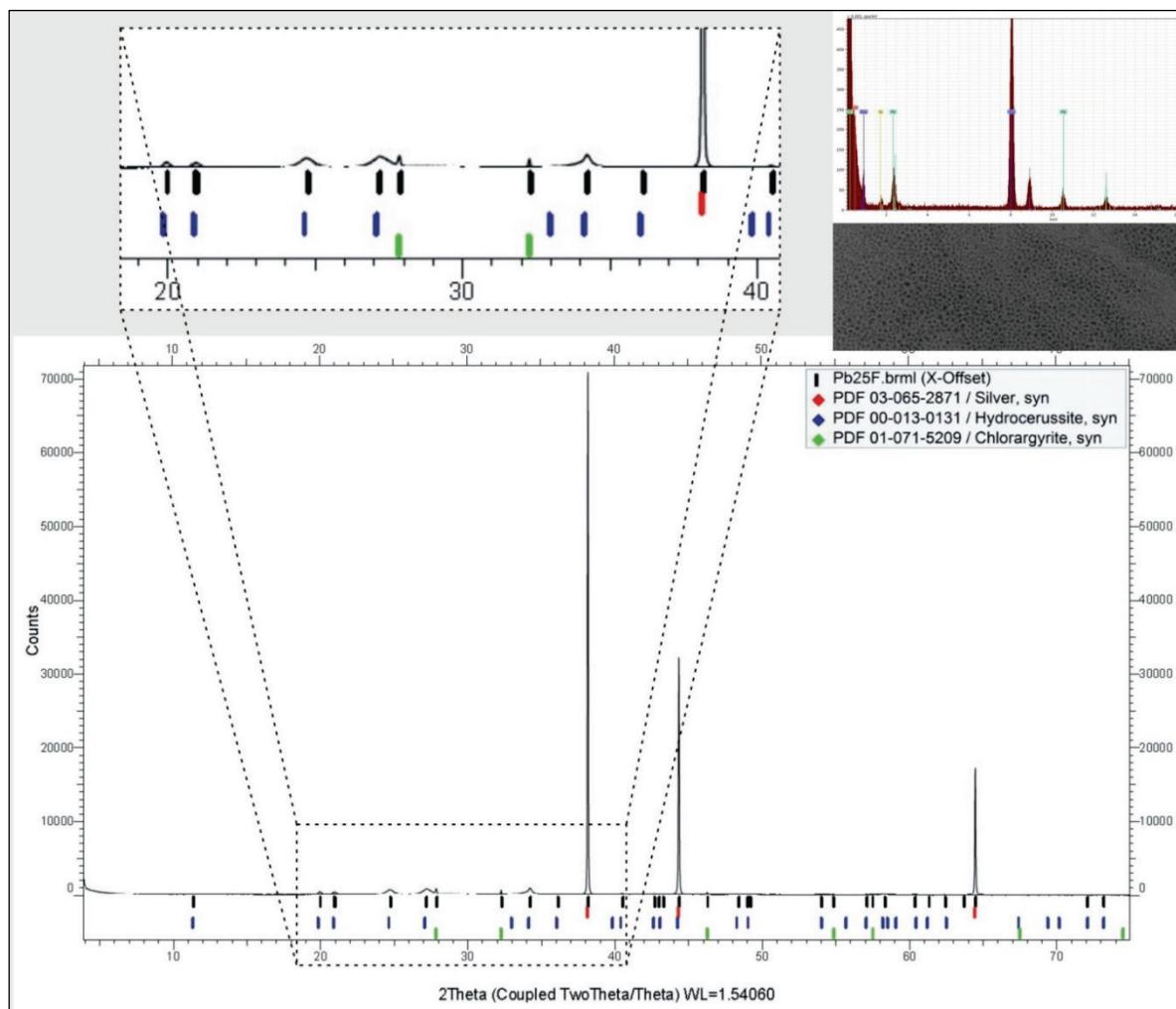
The method intercomparison studies will be conducted both under summer and winter conditions at both sites lasting 2 weeks each. By pooling the instruments and expertise of the two partners, BC will be measured on-line with the MAAP and the aethalometer techniques and from filter samples with the integrating sphere technique; EC will be investigated both from bulk samples with a Sunset Analyzer set both in reflection and transmission modes with three thermal protocols (NIOSH, DRI, EUSAAR2) and quasi on-line with two Sunset Field Analyzers set to two different temperature protocols. BrC will be analyzed with the modified integrating sphere technique. Background information on the aerosol will be obtained in parallel.

Study of transport of inhaled nano-sized particles (Pb, Cd) and their allocation in organs

(J. Smolík, smolik@icpf.cas.cz; supported by GACR, project No. 503/11/2315)

All of the evidence from animal and human studies showed that there are risks associated with inhalation of nano-sized particles (NSP). The alveolar translocation of NSP is likely the pathway how NSP can be transposed from air to the blood vessels, and distributed throughout

the body to organs. In spite of the fact that an extrapulmonary translocation is highly dependent on particle surface characteristics/chemistry, in addition to particle size, the study of transport of inhaled nano-particles Pb, Cd (elements, oxides), their allocations in organs, as well as study of toxicity these nanoparticles will be carried out with nanoparticles (10, 20 and 60 nm). The nonbiogenous elements (Cd, Pb) have been selected as products of technological processes and due to their presence in ambient aerosol. The research will give us more information for a proper understanding of risks of technologies producing Cd and Pb nano-sized particles and ambient aerosol risk.



XRD spectrum and TEM image with EDS spectrum (inset) of Pb nanoparticles generated by PVD method. Notice the effect of atmosphere (O_2 , CO_2 and humidity) during two weeks between synthesis and XRD analysis on the change of composition from Pb to hydrocerussite $[Pb_3(CO_3)_2(OH)_2]$

Methodology of evaluation of air quality effect on library and archival collections

(J. Smolík, smolik@icpf.cas.cz; supported by the Ministry of Culture of the CR, project No. DF11P01OVV020)

The aims of the project are: a) development of evaluation methods for indoor air quality in libraries and archives, targeted at reduction of damages on library and archival collections caused by adverse effects of environment and b) gaining detailed knowledge of direct dependences between damage of library and archival collections and surrounding environment, leading to precautions reducing the adverse effects of deteriorated environment. [Refs. 14, 16]



Particle number concentrations measured at library of Regional Museum at Teplice

Preparation of thin layers of ferromagnetic semiconductors

(R. Fajgar, fajgar@icpf.cas.cz; supported by ICPF)

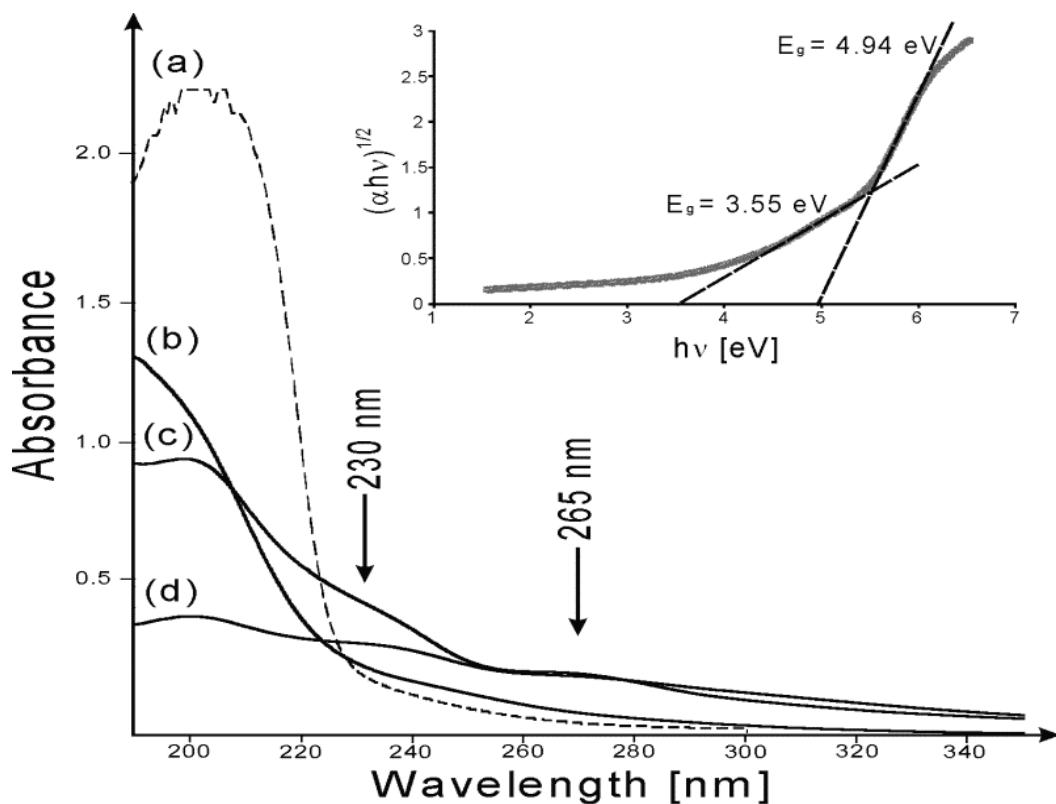
Manganese atoms diluted in silicon or germanium matrix are potential ferromagnetic semiconductors. Thin layers have been prepared by reactive excimer laser ablation of elemental manganese target under low pressure of volatile precursors (silane or germane). Ablated atoms with high energy (estimated initial temperature 1 mm above the Mn target surface is 1.9 eV) interact with gas and amorphous thin layers of Mn/Si or Mn/Ge are deposited. The prepared layers contain up to 40 % of Mn atoms. Successful crystallization was achieved by annealing of Mn/Si at as high temperatures as 1100°C or rapid laser annealing using TEA CO₂ laser. Magnetic properties were studied by SQUID technique, and weak ferromagnetic properties have been revealed so far.

RIR MAPLE Procedure for Deposition of Carbon Rich Si/C/H Films

(V. Dřínek, drinek@icpf.cas.cz; supported by GACR, project No. 13-25747S)

We applied the Resonant Infrared Matrix Assisted Pulsed Laser Evaporation (RIR MAPLE) technique to demonstrate a new approach to a controlled deposition of carbon rich amorphous Si/C/H film. In absence of radicals and accelerated species commonly generated in PECVD and sputtering setups, the RIR MAPLE method does not decompose precursor molecules. Moreover, unlike the standard MAPLE procedure, in which solvent molecules absorb laser energy from excimer or near infrared lasers, we applied the pulsed TEA CO₂ laser to excite the dendrimer precursor molecules in a frozen target. In this manner we achieved just cross-linking of the starting precursor on substrates and the deposition of carbon rich Si/C/H film. The film was analyzed by FTIR, UV/VIS, Raman and X-ray Photoelectron (XPS) spectroscopy and Atomic Force Microscopy (AFM) technique. According to analyses the film retained the precursor elemental composition free of graphitic (sp^2) clusters. In course of reaction only the peripheral allyl groups containing C=C bonds were opened to achieve cross-linking. Whereas annealing to 300 °C was necessary for the elimination of =C-H bonds in the films prepared at 200 °C, those bonds vanished completely in the films prepared at

substrate temperature 255 °C. The film possesses a smooth surface with Root Mean Square (RMS) parameter up to 10 nm within scanned distance 2.5 μm. [Ref. 7]



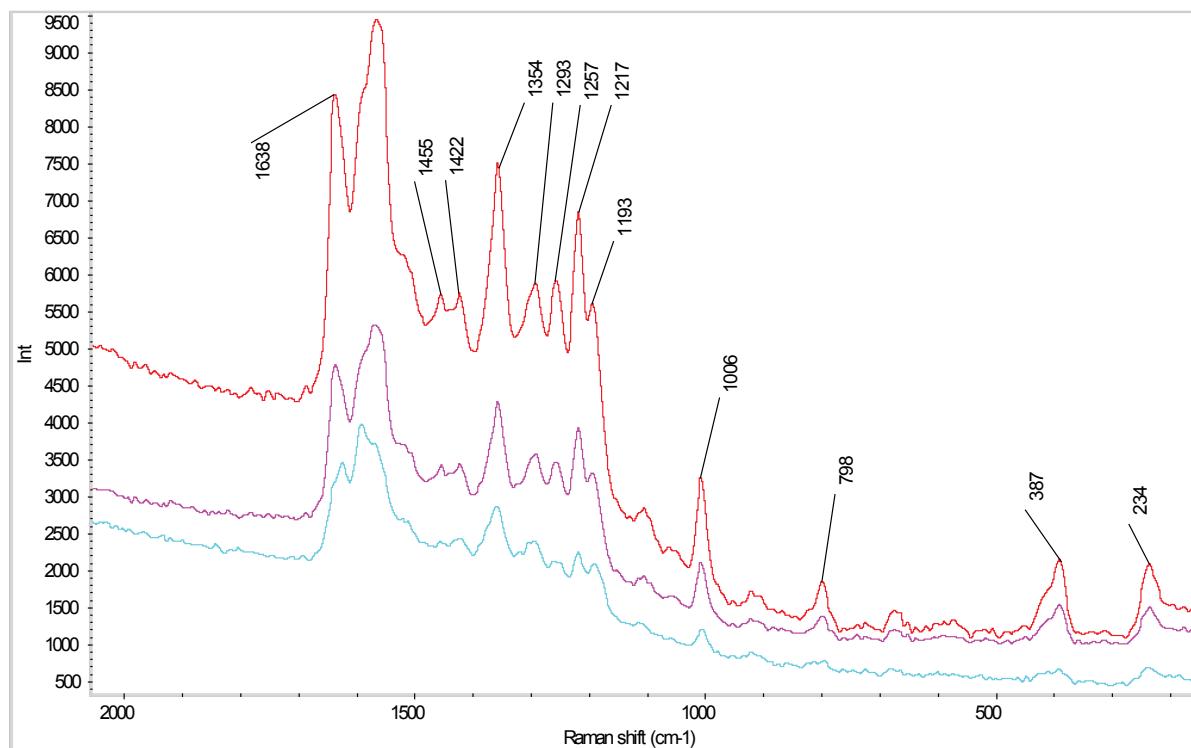
**UV/VIS spectra of the (a) precursor and film prepared at 255 °C
(b) before annealing and after annealing at (c) 400 and
(d) 500 °C. The Tauc plot of the spectrum (b) is depicted
in the inset with indicated energy gaps**

Novel sensors based on laser ablated graphene

(R. Fajgar, fajgar@icpf.cas.cz; supported by NATO, project No. 984399)

Graphene layer deposited by excimer laser ablation technique on a glass substrate was covered with silver nanoparticles and highly sensitive substrates for Surface-Enhanced Raman Scattering (SERS) were prepared. In vacuum, Ag nanoparticles reaching the polymer/graphene substrates induce graphitization of the graphene sheets as revealed by Raman spectroscopy. Ablation conditions were optimized to preserve graphene layers as a substrate for Ag nanoparticles deposition in helium atmosphere. The nanocomposites were characterized by means of spectroscopy, microscopy and diffraction techniques.

The SERS substrate performance was tested using Rhodamine 6G as a probe compound. Highly enhanced signal was observed and sensoric properties of the novel substrates were demonstrated. The substrates were optimized for detection of compounds, interesting from technological and medical aspects (e.g. methylviolet B, arsenazo, beryllon).



SERS spectra of beryllon, concentration 10⁻⁴, 10⁻⁵, 10⁻⁶ mol L⁻¹ (from top to bottom)

Laser-induced approach to nanoscopic titanium oxycarbides

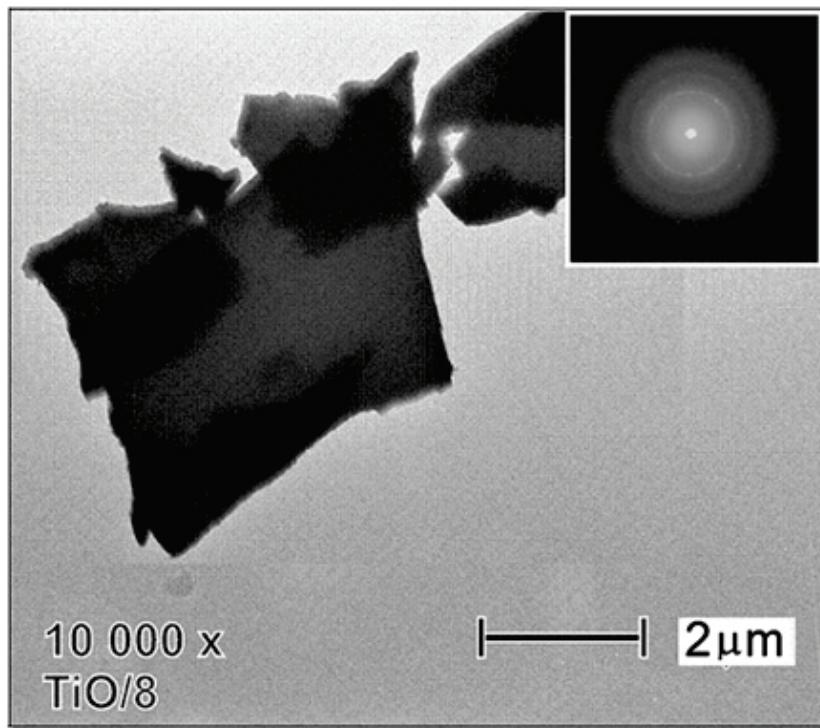
(J. Pola, pola@icpf.cas.cz and V. Jandová, jandova@icpf.cas.cz; supported by ICPF)

IR laser-induced reactive ablation of different targets (elemental titanium, titanium monoxide and titanium ethoxide) was carried out. Ablation of hexagonal titanium in vacuum leads to amorphization of ablated Ti particles and when carried out in gaseous carbon monoxide it proceeds as reactive ablation involving particles amorphization, oxidation and carbidation.

The ablation of titanium monoxide in hydrogen was compared to the same process induced in vacuum and shown to result in deposition of hydrated surface modified nanostructured titanium suboxide films. The films exert good adhesion to metal and quartz surfaces and are hydrophobic in spite of having their surface coated with adsorbed water.

Reactive IR ablation of a frozen titanium ethoxide target (-100°C) in gaseous methane (2 to 15 Pa) proceeds as oxidation and carbidation process affording films with good adhesion and various hydrophilicity depending on carbon content.

The films were examined by FTIR, Raman and X-ray photoelectron spectroscopy, X-ray and electron diffraction and electron microscopy. [Refs. 2, 3, 6]



TEM image of the solid Ti/O/C film deposited in methane (8 Pa). Inset: the electron diffraction pattern, showing nanocrystalline structure of the film

Quantum size effect in semiconductor nanostructures for optoelectronics

(R. Fajgar, fajgar@icpf.cas.cz; V. Dřínek drinek@icpf.cas.cz; cooperation with Institute of Physics of the ASCR, supported by MEYS, project No. LH12236)

Thin layers of hydrogenated silicon were prepared by excimer laser ablation of silicon target in vacuum and silane (SiH_4) atmosphere. Optical and electrical properties were studied for potential applications in light emitting devices and photovoltaic cells. Introducing of inorganic nanoparticles (PbS , Mg_2Si) into silicon layers was studied with aim to increase light scattering and absorption in solar cells. Reflection and fluorescence spectra confirm the improved light scattering of layers with embedded nanoparticles. Enhancement of optical absorption, especially at lower wavelengths was demonstrated. Combination of standard RF plasma-enhanced CVD in two electrodes configuration with reactive excimer laser ablation afforded multilayers of Mg_2Si nanoparticles encapsulated in amorphous silicon. The multilayers show an enhanced absorption in Vis-NIR spectral region. [Ref. 5]

International co-operations

Division of Nuclear Physics, Department of Physics, Lund University, Lund, Sweden
Finnish Meteorological Institute, Helsinki, Finland: Studies on homogeneous nucleation using diffusion chambers

Ghent University, Institute for Nuclear Sciences, Ghent, Belgium: OC/EC in urban and suburban PM10 aerosol in Prague, Hygroscopic properties of urban and suburban carbonaceous aerosols

Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan
Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Switzerland
Norwegian Institute for Air Research, Kjeller, Norway: Indoor aerosol behavior

Southern Illinois University Carbondale, Carbondale, IL, USA: Friction materials based on polymer matrix containing metals and their impact on environment
Technical University of Crete, Chania, Greece: Aerosols in the indoor environment
University of Helsinki, Division of Atmospheric Sciences, Helsinki, Finland
Tampere University of Technology, Tampere, Finland: Synthesis and characterization of nanosized metal/ceramic particles
University of Vienna, Faculty of Physics, Dept. of Aerosol physics and Environmental Physics, Vienna, Austria: Black and elemental carbon analysis, aerosol optical properties
Faculty of Technology and Metallurgy, University of St. Cyril & Methodius, Skopje, Republic of Macedonia: Preparation of SERS active substrates based on Ag/graphene
Instituto de Estructura de la Materia, CSIC, Madrid, Spain: Studies on IR laser deposition of nanosized metal chalcogenides, polycarbosilathianes and Ti based nanostructures
King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia: Preparation of Ag/C nanocomposites by laser-induced carbonization of n-hexane
Southeast University, Department of Physics, Nanjing, China: Preparation of Ag/C nanocomposite by laser-induced carbonization of n-hexane
National Institute for Lasers, Plasma and Radiation Physics, Bucharest, Romania: Laser-induced CVD of Fe/polymer nanocomposites
National Institute of Advanced Industrial Research and Technology, Tsukuba, Japan: Laser control of organic reactions
POLYMAT, Institute for Polymer Materials, San Sebastian, Spain: Laser ablation of graphene-based composites
AC2T, Wiener Neustadt, Austria: Tribological study of nanostructured materials (nanowires, nanoplatelets)
Institute of Automation and Control Processes of FEB RAS, Vladivostok, Russia: Deposition of magnesium silicide nanoparticles encapsulated in amorphous silicon
Institute of Atmospheric Pollution Research, Monterotondo, Italy: Gaseous pollutants

Visits abroad

D. Brus: Finnish Meteorological Institute, Helsinki, Finland (12 months)
L. Krabáč: AC2T, Austria (4 months)

Visitors

T. Hussein, University of Helsinki, Helsinki, Finland
V. Nororos, University of Helsinki, Helsinki, Finland
Gordana Siljanoska, University of St. Cyril & Methodius, Skopje, R. Macedonia
Nikolay G. Galkin, Inst. of Automation and Control Proc. of FEB RAS, Vladivostok, Russia
A. Wonaschütz, University of Wien, Faculty of Physics

Teaching

V. Ždímal: Faculty of Mathematics and Physics, Charles University in Prague, undergraduate course: "Aerosol Engineering"
V. Ždímal: ICT, Faculty of Chemical Engineering, graduate course "Aerosol Engineering"

Publications

Original papers

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Chapters in books

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